Isomerisatie van nitrophenylsulfonylureumderivaten

Groot, Jacob

SUMMARY.

This thesis describes the preparation of derivatives of nitrophenylsulphonyl urea and isourea and the decomposition of the o- and p-nitro compounds under the influence of alkali. This decomposition is an intramolecular isomerization followed by loss of sulphur dioxide:

$$NO_2C_6H_4SO_2NHCONHR \rightarrow NO_2C_6H_4N(R)CONHSO_2H \rightarrow NO_2C_6H_4N(R)CONH_2 + SO_2$$

The derivatives of isourea, when heated with alkali, also lose sulphur dioxide, but moreover the ether function is disrupted and urea derivatives are formed:

$$NO_2C_6H_4SO_2N : C(OCH_3)NH_2 \xrightarrow{H_2O} NO_2C_6H_4NHCONH_2 + CH_3OH + SO_2$$

This hydrolysis is also known for O,N,N-trimethylisourea, which compound is decomposed by boiling water into dimethylurea and methyl alcohol.

It is probable that the derivatives of nitrophenylsulphonylisourea first isomerise with loss of sulphur dioxide, after which the isourea derivative formed decomposes into a derivative of urea and methyl alcohol. This supposition is confirmed by the fact that the isomerization of N-p-nitrophenylsulphonyl-O-methylisourea is faster than that of p-nitrophenylsulphonylurea. This would not be the case, should the first step be the formation of a sulphonylurea derivative.

On p. 50 a survey is given of all the compounds for which the behaviour in the presence of hot alkali has been examined; the second column mentions the decomposition products.

The compounds with a meta nitro group do not undergo an isomerization. The presence of an o- or p-nitro group is necessary to weaken the bond between the sulphonyl group and the benzene nucleus.

In the presence of an excess of alkali the isomerization is a monomolecular reaction. A reaction mechanism is proposed (p. 53); the accelerating influence of the methyl and phenyl groups is ascribed to a reduction of the activation energy, necessary for the rupture of the carbon sulphur bond. Indeed it was found that this energy is diminished by the introduction of these groups.